

**DIVIDED PRESSURE VESSEL APPARATUS  
FOR CARBON DIOXIDE BASED SYSTEMS  
AND METHODS OF USING SAME**

**Related Application**

This application claims the benefit of United States Provisional Application Number 60/240,473, filed October 13, 2000, the disclosure of which is incorporated herein by reference in its entirety.

**Field of the Invention**

This invention relates to densified gas based systems, more particularly to divided pressure vessel apparatus for carbon dioxide based systems and methods of using same.

**Background of the Invention**

An important operational consideration for many, if not all, carbon dioxide processing systems is throughput, which may be defined as the amount of articles or materials that may be processed in a given period of time. In various processes that utilize carbon dioxide as a solvent, multiple solvent baths may be used to improve operational efficiency by increasing throughput. For example, in a carbon dioxide based dry cleaning system, it may be desirable to provide pre-washing, washing, rinsing, and distillation operations. The pre-wash, wash, and rinse solutions may each have a different chemical composition. If a single tank were used to store the various baths, the composition of the solution in the tank would need to be adjusted between

each operation, which may increase cycle time and decrease throughput. By utilizing a tank for storing a pre-wash solution, a separate tank for storing wash solution, another separate tank for storing a rinse solution, and yet another separate distillation tank, the dry cleaning system may be able to cycle through the operations of pre-  
5 washing, washing, rinsing, and distillation in a more timely manner.

U.S. Patent No. 5,267,455 to Dewees et al. proposes a dry cleaning system particularly suited for employing supercritical carbon dioxide as the cleaning fluid consisting of a sealable cleaning vessel containing a rotatable drum adapted for holding soiled substrate, a cleaning fluid storage vessel, and a separate gas vaporizer  
10 vessel for recycling used cleaning fluid.

While utilizing multiple solvent baths in carbon dioxide based systems may improve operational efficiency, the increased capital costs associated with such systems may outweigh some of the operational benefits. Carbon dioxide based systems may be required to operate at elevated pressures in order to maintain the  
15 carbon dioxide solvent in either a liquid or a supercritical state. As a result, each of the separate tanks must be a stamp coded and certified pressure vessel, which can be quite expensive. Additionally, each of the separate tanks must be in constant fluid communication with a pressure relief valve. Thus, the capital cost of constructing a carbon dioxide based system having multiple solvent baths may outweigh some, if not  
20 all, of the operational benefits that may be gained by utilizing such a system.

WO 97/33031 proposes a storage/still vessel that both distills and stores the liquid gas for use in another cleaning cycle. The storage/still vessel includes a tube located within an inner cavity of an outer tank. At the top of the tube is an opening that provides fluid communication between the inner cavity and an inner chamber of  
25 the tube. The bottom of the tube has a one-way control valve that allows the liquid gas to flow from the inner cavity to the inner chamber. The vessel has a heating element that can heat and vaporize the liquid gas within the inner chamber of the tube. The still vaporizes the liquid gas within the tube, which causes liquid to flow from the inner cavity to the inner chamber. Vaporized liquid gas condenses and falls into the  
30 inner cavity, which then forms a layer of distilled "clean" liquid, on top of a layer of undistilled "dirty" liquid. The cycle is continued until the level of dirty liquid falls below the one way control valve.

WO 97/33031 does not provide an apparatus utilizing a carbon dioxide based solvent that will allow two or more fluids having different chemical compositions to

be stored and/or processed within the same pressure vessel while maintaining the different chemical compositions of the two or more fluids.

### **Summary of the Invention**

5           According to the present invention, divided pressure vessels for use in a carbon dioxide based system are provided. Divided pressure vessels of the present invention may allow multiple solvent baths each having a different chemical composition to be stored and/or processed in a single pressure vessel while maintaining the different chemical compositions of the multiple solvent baths. Thus, 10 divided pressure vessels of the present invention may provide the improved operational efficiency of a carbon dioxide based system having multiple solvent baths while decreasing the capital costs that may be associated with such systems. Methods of utilizing such divided pressure vessels in processing systems employing carbon dioxide based solvents are also be provided.

15           According to the present invention, methods of utilizing a divided storage vessel include transferring a first densified gas based treating solution from a first liquid chamber in a divided storage vessel having a plurality of liquid chambers to a processing vessel, returning the first treating solution from the processing vessel to the divided storage vessel, transferring a second carbon dioxide based treating 20 solution having a composition different from the first treating solution from a second liquid chamber in the divided storage vessel to a processing vessel, and returning the second treating solution from the processing vessel to the divided storage vessel. The processing system may be a batch processing system, a semi-batch processing system, or a continuous processing system.

25           In embodiments of the present invention, the methods of utilizing a divided storage vessel include contacting an article in the processing vessel with the first treating solution, and contacting the article in the processing vessel with the second treating solution. The first treating solution may be a pre-wash solution, a wash solution, or a coating solution, and the second treating solution may be a wash 30 solution, a coating solution, or a rinse solution. The articles may be various substrates including, but not limited to, fabric substrates, metal substrates, and electronic devices, to name just a few. The operation of contacting the article with the wash solution may include removing polymeric materials, such as resins, adhesive, coatings, and inks, from the article.

In other embodiments of the present invention, at least one of the first or second treating solutions is an impregnating solution that includes an impregnating agent. The operation of contacting the article with the impregnating solution includes impregnating the article with the impregnating agent. The article may be a porous material and the impregnating agent may be insect treatments, pigments, strength enhancers, water repellants or pollution repellants.

In still other embodiments of the present invention, at least one of the first or the second treating solutions is an extracting solution, and the operation of contacting the article with the extracting solution includes extracting a substance from the article using the extracting solution.

In yet other embodiments of the present invention, at least one of the first or the second treating solutions is a developing solution. The operation of contacting the article with the developing solution includes developing a resist on a semiconductor substrate using the developing solution.

In other embodiments of the present invention, the methods of utilizing a divided storage vessel includes the operation of synthesizing a chemical compound by combining the first treating solution with the second treating solution. The first treating solution is a first reacting solution that includes a first reactant and the second treating solution is a second reacting solution that includes a second reactant.

In still other embodiments of the present invention, the methods of utilizing a divided storage vessel includes polymerizing one or more monomers by combining the first treating solution with the second treating solution where the first treating solution includes a first monomer and the second treating solution includes an initiator or a second monomer.

In yet other embodiments of the present invention, the methods of utilizing a divided storage vessel includes purifying a chemical compound by combining the first treating solution comprising the chemical compound with a third treating solution substantially devoid of liquid carbon dioxide.

Cleaning methods are also provided by the present invention. Cleaning methods according to the present invention include transferring a first densified gas based treating solution from a first liquid chamber of a divided working tank to a wash tank containing an article, contacting the article with the first liquid, returning the first treating solution from the wash tank to the divided working tank, transferring a second densified gas based treating solution from a second liquid chamber of the

divided working tank to the wash tank, contacting the article with the second treating solution, and returning the second treating solution from the wash tank to the divided working tank. The method may include storing a plurality of densified gas based treating solutions present as two-phase systems in a divided storage vessel having a plurality of liquid chambers that share a common vapor space.

Dry cleaning methods are also provided by the present invention. Dry cleaning methods according to the present invention include transferring a first densified gas based dry-cleaning solution from a first liquid chamber of a divided working tank to a wash tank containing a dry-cleanable article, contacting the dry-cleanable article with the first liquid, returning the first dry-cleaning solution from the wash tank to the divided working tank, transferring a second densified gas based dry-cleaning solution from a second liquid chamber of the divided working tank to the wash tank, contacting the dry-cleanable article with the second dry-cleaning solution, and returning the second dry-cleaning solution from the wash tank to the divided working tank. The method may include storing a plurality of densified gas based dry-cleaning solutions present as two-phase systems in a divided storage vessel having a plurality of liquid chambers that share a common vapor space.

In embodiments of the present invention, the first dry-cleaning solution is a pre-wash solution, a wash solution, or a coating solution, and the second dry-cleaning solution is a wash solution, a coating solution, or a rinse solution.

In other embodiments of the present invention, the operation of returning the first dry-cleaning solution from the wash tank to the divided working tank includes returning the first dry-cleaning solution from the wash tank to the first chamber of the divided working tank. The operation of returning the second dry-cleaning solution from the wash tank to the divided working tank includes returning the second dry-cleaning solution from the wash tank to the second chamber of the divided working tank. The second liquid may be distilled in the second liquid chamber to form still bottoms and vapor consisting essentially of carbon dioxide.

In still other embodiments of the present invention, dry cleaning methods include transferring a first volume of the first dry-cleaning solution from the first liquid chamber into a third liquid chamber of the divided working tank before transferring a first dry-cleaning solution from the first liquid chamber to the wash tank. The operation of transferring a first volume includes equilibrating the liquid levels in the first liquid chamber and the third liquid chamber. The dry cleaning



methods include contacting the article with the pre-wash solution, and returning the pre-wash solution from the wash tank to the third liquid chamber of the divided working tank before transferring a first dry-cleaning solution from the first liquid chamber to the wash tank. The pre-wash solution may be distilled in the third liquid chamber. The distilling operation may occur during at least one of the foregoing operations. The operation of returning the second dry-cleaning solution from the wash tank to the divided working tank may include returning the second dry-cleaning solution from the wash tank to the first liquid chamber.

A divided working tank for use in a carbon dioxide based system is also provided by the present invention. The divided working tank includes an exterior wall defining an interior volume and capable of withstanding an internal pressure of at least about 500 psig, a first dividing member extending from an interior surface of the exterior wall and defining a first and a second liquid chamber in the divided pressure vessel, the first and the second liquid chambers sharing a common vapor space, and a first treating solution consisting essentially of densified gas positioned in the first liquid chamber. The densified gas is preferably liquid carbon dioxide.

In embodiments of the present invention, the divided working tank includes a second dividing member defining a third liquid chamber. The third liquid chamber shares the common vapor space with the first and the second liquid chambers. The second liquid chamber is positioned between the first liquid chamber and the third liquid chamber. A heating element is operatively associated with the third liquid chamber.

In other embodiments of the present invention, the divided working tank includes a first opening in the exterior wall adjacent the first liquid chamber for liquid transfer into and/or out of the first liquid chamber, a second opening in the exterior wall adjacent the second liquid chamber for liquid transfer into and/or out of the second liquid chamber, a third opening in the exterior wall adjacent the third liquid chamber for liquid transfer into and/or out of the third liquid chamber, and a fourth opening in the exterior wall adjacent the common vapor space for fluid transfer into and/or out of the common vapor space. The fourth opening is preferably positioned above the third liquid chamber.

In still other embodiments of the present invention, the divided working tank includes a second densified gas based treating solution positioned within the second

liquid chamber. The first and the second treating solutions have different compositions.

A dry cleaning system employing a carbon dioxide based solvent is also provided by the present invention. The dry cleaning system includes a divided working tank configured to store a plurality of densified gas based dry-cleaning solutions having different compositions as described above and a wash tank configured to contact a dry-cleanable article to be cleaned with one or more of the plurality of dry-cleaning solutions. The wash tank is in fluid communication with the divided working tank.

In embodiments of the present invention, the cleaning system may include a liquid transfer system that provides liquid communication between the divided working tank and the wash tank, and a vapor transfer system that provides vapor communication between the divided working tank and the wash tank. The first, the second, and the third openings of the divided working tank may be in liquid communication with the liquid transfer system. The fourth opening of the divided working tank may be in fluid communication (i.e., liquid and/or vapor communication) with the vapor transfer system. The vapor transfer system may include a condenser that is in fluid communication with the fourth opening of the exterior wall of the divided working tank.

In embodiments of the present invention, methods of utilizing a divided storage vessel include transferring a first treating adjunct from a first chamber in a divided storage vessel having a plurality of chambers that share a common vapor space to a processing vessel, transferring a densified fluid comprising a liquid densified gas or a supercritical fluid into the processing vessel, removing the first treating adjunct from the processing vessel, transferring a second treating adjunct having a composition different from the first treating adjunct from a second chamber in the divided storage vessel to the processing vessel, and removing the second treating adjunct from the processing vessel.

In other embodiments of the present invention, methods of utilizing a divided storage vessel include charging a first densified fluid comprising a liquid densified gas or a supercritical fluid into a processing vessel, removing the first densified fluid from the processing vessel, charging the first densified fluid into a first liquid chamber in a divided storage vessel having a plurality of liquid chambers that share a common vapor space, charging a second densified fluid comprising a liquid densified



gas or a supercritical fluid into the processing vessel, removing the second densified fluid from the processing vessel, and charging the second densified fluid into a second liquid chamber in the divided storage vessel.

Methods and apparatus according to the present invention may therefore provide the operational efficiency associated with a densified gas based processing system having multiple solvent baths stored in various separate tanks at a lower capital costs than such processing systems. It will be understood that the present invention may be embodied as methods and apparatus and combinations thereof.

### **Brief Description of the Drawings**

**Figure 1** is a front section view of a divided pressure vessel according to the present invention having a horizontal orientation;

**Figure 2** is an end section view taken along line 2-2 of the vessel of **Figure 1**.

**Figure 3** is a front section view of a divided pressure vessel according to the present invention having a vertical orientation;

**Figure 4A** is a top section view taken along line 4A-4A of the vessel of **Figure 3**;

**Figure 4B** is a top section view taken along line 4B-4B of the vessel of **Figure 3**;

**Figure 5** is a schematic diagram illustrating embodiments of a processing system according to the present invention employing a carbon dioxide based solvent and having a divided pressure vessel;

**Figure 6** is a schematic diagram illustrating embodiments of a batch processing system according to the present invention employing a carbon dioxide based solvent and having a divided working tank;

**Figure 7** is a schematic diagram illustrating embodiments of a purification and isolation system according to the present invention; and

**Figure 8** is a schematic diagram illustrating embodiments of a batch processing system according to the present invention having a divided adjunct addition tank and a divided waste collection tank.

### **Detailed Description of Preferred Embodiments**

The present invention now will be described more fully hereinafter with reference to the accompanying drawings, in which preferred embodiments of the

invention are shown. This invention may, however, be embodied in many different forms and should not be construed as limited to the embodiments set forth herein; rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art.

5 As used herein, "fluid communication" means liquid and/or vapor communication. As used herein, "densified gas" means a liquid fluid that is gaseous at ambient conditions. Examples include carbon dioxide, helium, nitrogen, air, methane, ethane, propane, butane, ammonia, and nitrous oxide. Preferably, the densified gas is carbon dioxide. As used herein, "densified fluid" means a liquid or supercritical fluid that is  
10 gaseous at ambient conditions. Examples include carbon dioxide, helium, nitrogen, air, methane, ethane, propane, butane, ammonia, and nitrous oxide. Preferably, the densified fluid is carbon dioxide.

Referring first to **Figures 1 and 2**, an embodiment of a divided pressure vessel **100** according to the present invention having a cylindrical configuration and a  
15 horizontal orientation will now be described. The divided pressure vessel **100** has an exterior wall **110** defining a cylindrical interior volume **118**. While the embodiment illustrated in **Figure 1** shows an exterior wall **110** defining a cylindrical interior volume **118**, it is to be understood that exterior walls of the present invention may define various other shapes of interior volumes including, but not limited to, spherical  
20 and cubic, which includes rectangular.

As illustrated in **Figure 1**, the exterior wall **110** includes a longitudinally extending side wall member **112**, a first end wall member **114**, and a second end wall member **116**. The side wall member **112** extends circumferentially to define an interior volume **118**. As illustrated by the embodiment of **Figure 2**, the side wall  
25 member **112** extends circumferentially to form a divided pressure vessel having a cylindrical interior volume with a circular lateral cross-section. However, it is to be understood that side wall members of the present invention may extend circumferentially to form divided pressure vessels of the present invention having various lateral cross-sections including rectangular cross-sections, among others. As  
30 used herein, the term "rectangular" encompasses square cross-sections. While the embodiment illustrated in **Figure 1** shows a side wall member **112** having a substantially straight longitudinal cross-section, it is to be understood that side wall members according to the present invention may have various other longitudinal cross-sections, including but not limited to arcuately shaped cross-sections. Side wall

members and first and second end wall members according to the present invention may be arcuately shaped to define a spherical interior volume.

As shown in **Figure 1**, the side wall member **112** has a first end portion **111** and a second end portion **113** longitudinally spaced from the first end portion **111**.

5 The first end wall member **114** is coupled to the first end portion **111** of the side wall member **112**. The second end wall member **116** is coupled to the second end portion **113** of the side wall member **112**. Although the embodiment of **Figure 1** shows first and second end wall members **114** and **116**, respectively, having a generally arcuate shape, it is to be understood that end wall members of the present invention may have  
10 various other shapes including, but not limited to, planar.

As illustrated in **Figure 1**, a first dividing member **120** extends from an interior side of the exterior wall **110**. The first dividing member **120** defines a first chamber **131** and a second chamber **132** within the divided pressure vessel **100**. The first chamber **131** and the second chamber **132** share a common vapor space **135**. A  
15 second dividing member **122** is longitudinally spaced from the first dividing member **120** and extends from the interior side of the exterior wall **110**. The second dividing member **122** defines a third chamber **133** within the divided pressure vessel **100**. The third chamber **133** shares the common vapor space **135** with the first and the second chambers **131** and **132**, respectively.

20 Although the embodiment illustrated in **Figure 1** shows the dividing pressure vessel **100** having first and second dividing members **120** and **122**, respectively, it is to be understood that divided pressure vessels of the present invention may have fewer or more dividing members, although two dividing members are preferred. While the embodiment of the divided pressure vessel illustrated in **Figure 1** shows  
25 first and second dividing members **120** and **122**, respectively, that only extend a portion of the way across the divided pressure vessel **100**, it is to be understood that dividing members according to the present invention may extend completely across the divided pressure vessels. However, when a dividing member according to the present invention extends completely across the divided pressure vessel, a line or  
30 other vapor passage structure should connect the vapor spaces of the adjacent chambers defined by the dividing member such that the vapor spaces of the adjacent chambers may not be isolated from one another. Thus, the adjacent chambers will still share a common vapor space, and the pressure in each chamber will be the same. Dividing members of the present invention are preferably built to withstand the

hydrostatic pressure of the dry-cleaning solution(s) contained in the liquid chambers adjacent the dividing member, but not to withstand system pressure. Thus, divided pressure vessels of the present invention may reduce the capital costs associated with providing a multi-bath system. Although the embodiments illustrated in **Figure 1**

5 show a horizontally oriented divided pressure vessel **100** having substantially vertically oriented dividing members **120** and **122**, it is to be understood that horizontally oriented divided pressure vessels of the present invention may have dividing members that are oriented other than vertically. For example, embodiments of horizontally oriented dividing members are described below with reference to  
10 **Figures 3 and 4.**

As shown in **Figure 1**, the first and the second dividing members **120** and **122**, respectively, are continuous members that preclude internal liquid communication through the dividing members. As used herein, "internal liquid communication" is liquid communication that occurs within the divided pressure vessel. Put another  
15 way, the first and the second dividing members **120** and **122**, respectively, are impermeable to liquid carbon dioxide solutions. Thus, a liquid carbon dioxide solution may be stored in one chamber without contaminating another liquid carbon dioxide solution that is stored in an adjacent chamber. As a result, a first liquid solution contained in the first chamber **131** may include one or more constituents that  
20 are different from the constituents in a second liquid solution contained in the second chamber **132**. For example, the first liquid solution may consist of liquid carbon dioxide while the second liquid solution contains one or more cleaning adjuncts. While the embodiments illustrated in **Figure 1** show first and second dividing members **120** and **122** as continuous members, it is to be understood that dividing  
25 members of the present invention may be discontinuous members (e.g., a valve may reside in the dividing member), although continuous members are preferred. If the dividing member is discontinuous having a valve residing therein, it is preferable that the valve is a two-way valve.

As illustrated in **Figure 1**, several openings in the exterior wall **110** of the  
30 divided pressure vessel **100** allow fluid transfer into and/or out of the divided pressure vessel **100**. A first opening **151** in the exterior wall **110** is adjacent the first liquid chamber **131**. The first opening **151** may be used for liquid transfer into and/or out of the first liquid chamber **131**. A second opening **152** in the exterior wall **110** is adjacent the second liquid chamber **132** and may be used for liquid transfer into

and/or out of the second liquid chamber 132. A third opening 153 in the exterior wall 110 is adjacent the third liquid chamber 133. The third opening 153 may be used for liquid transfer into and/or out of the third liquid chamber 133. A fourth opening 154, a fifth opening 155, and a sixth opening 156 in the exterior wall 110 are adjacent the common vapor space 135. The fourth, the fifth, and the sixth openings 154, 155, and 156, respectively, may be used for vapor transfer into and/or out of the common vapor space 135. Additionally, the fourth opening 154 may also be used for liquid transfer into the first liquid chamber 131, the fifth opening 155 may also be used for liquid transfer into the second liquid chamber 132, and the sixth opening 156 may also be used for liquid transfer into the third liquid chamber 133.

While the embodiments illustrated in **Figure 1** show the first, the second, and the third openings 151, 152, and 153, respectively, positioned at the bottom of the divided pressure vessel 100, it is to be understood that openings that allow liquid transfer into and/or out of divided pressure vessels of the present invention may be positioned at other locations in the exterior wall that are below the liquid level.

Although the embodiments shown in **Figure 1** illustrate fourth, fifth, and sixth openings 154, 155, and 156, respectively, which allow vapor transfer into and/or out of the divided pressure vessel 100, it is to be understood that divided pressure vessels of the present invention may have as few as one such opening adjacent the common vapor space. When only one opening is provided, it is preferable that the opening be positioned above the third liquid chamber 133 (i.e., the sixth opening 156). While the embodiments illustrated in **Figure 1** show the fourth, the fifth, and the sixth openings 154, 155, and 156, respectively, positioned at the top of the divided pressure vessel 100, it is to be understood that openings that allow vapor transfer into and/or out of divided pressure vessels of the present invention may be positioned at other locations in the exterior wall that are above the liquid level (i.e., adjacent the common vapor space). While the embodiments illustrated in **Figures 1** show liquid and vapor inlets and outlets (first through sixth openings) that penetrate the exterior wall of the divided pressure vessel, it is to be understood that chamber inlets and outlets may be provided from one or more internal headers, where the one or more internal headers penetrate the exterior wall.

As illustrated in **Figure 1**, the first, the second, and the third openings 151, 152, and 153, respectively, are coupled to isolation valves 161, 162, and 163, respectively. As will be understood by those skilled in the art, isolation valves 161,

162, and 163 may be various types of valves including, but not limited to, ball, 2 or 3 way butterfly, gate, globe, or check valves, to name just a few. Although the embodiments illustrated in **Figure 1** show isolation valves 161, 162, and 163, it is to be understood that various isolation means known to those skilled in the art may be used, including, but not limited to, liquid fluid columns such as u-tubes, and pumps such as positive displacement pumps or rotary pumps with an upstream check valve.

As shown in **Figure 1**, the divided pressure vessel 100 contains various carbon dioxide based treating solutions. A first treating solution 141 resides in the first liquid chamber 131. A second treating solution 142 resides in the second liquid chamber 132, and a third treating solution 143 resides in the third liquid chamber 133. At least one of the first, the second, or the third treating solutions 141, 142, or 143, respectively, is a liquid carbon dioxide based treating solution. As used herein, "carbon dioxide based" treating solutions are treating solutions that comprise greater than 50% by volume liquid carbon dioxide. Preferably, at least two of the first, the second, or the third treating solutions 141, 142, or 143, respectively, are liquid carbon dioxide based treating solutions. More preferably, at least two treating solutions comprise greater than about 60% or 75% by volume, most preferably greater than about 90% by volume, liquid carbon dioxide and the remaining treating solution consists of or consists essentially of liquid carbon dioxide. Treating solutions of the present invention may also include various other materials that are specific to the particular processing application, as will be understood by those skilled in the art. For example, in dry cleaning applications, treating solutions of the present invention may be pre-wash solutions, wash solutions, coating solutions, or rinse solutions, among others, and may include detergents, bleaches, whiteners, softeners, sizing, starches, enzymes, hydrogen peroxide or a source of hydrogen peroxide, fragrances, and coating adjuncts, among other materials. In polymer synthesis applications, treating solutions may include various monomers and initiators, among other materials. In cleaning/processing of hard surfaces, treating solutions may include cleaning adjuncts, rinsing adjuncts, coating adjuncts, and passivation adjuncts, just to name a few. While the embodiments illustrated in **Figure 1** show treating solutions 141, 142, and 143, respectively, residing in each of the first, the second, and the third chambers 131, 132, and 133, respectively, it is to be understood that one or more chambers of the divided pressure vessels of the present invention may be devoid of carbon dioxide based treating solution.

As illustrated in **Figure 1**, the divided pressure vessel includes a heating element **170** operatively associated with the second chamber **132**. The heating element **170** is preferably a partial steam jacket, but may be various heating elements as will be understood by those skilled in the art. Although the embodiments illustrated in **Figure 1** show a single heating element **170**, it is to be understood that divided pressure vessels of the present invention may have multiple heating elements operatively associated with one or more chambers or may not include a heating element. While the embodiments illustrated in **Figure 1** show the heating element **170** as not penetrating the exterior wall **110**, it is to be understood that heating elements of the present invention that penetrate the exterior wall (e.g., an internal coil heater) are also operatively associated with a liquid chamber. However, heating elements that do not penetrate the exterior wall are preferred because, among other things, the integrity of the exterior wall is maintained and concerns about fouling and overpressurization of the heating system due to a defective internal coil can be reduced.

As shown in **Figure 1**, a single operating level sensor **180** is positioned within the divided pressure vessel **100**. More specifically, the level sensor **180** is positioned within the first liquid chamber **131**. The level sensor **180** is capable of sensing the level of carbon dioxide based treating solution in the first liquid chamber **131** and is used to control the upper liquid level in the first liquid chamber **131**. As will be understood by those skilled in the art, the level sensor **180** may be selected from various level sensors including, but not limited to, float-actuated devices, displacer-actuated devices, head devices, level-sensors that measure electrical characteristics (electrical devices) such as conductivity and capacitance, thermal devices, and sonic devices, among others. Preferably, the level sensor **180** is a non-mechanical level sensor (i.e. has no moving parts in contact with the liquid being measured) such as an electrical device, a thermal device, or a sonic device. More preferably, the level sensor **180** is an ultra sonic sensor. Most preferably, the level sensor **180** is a Sensall SE98-067, which is commercially available. Although multiple operating level sensors may be used, it is preferable to use a single operating level sensor instead of multiple operating level sensors to control the liquid levels in a divided pressure vessel having two or more liquid chambers. More preferably, only a single operating level sensor is used to control the liquid levels in a divided pressure vessel having three liquid chambers. By using a single operating level sensor rather than multiple

level sensors, the capital cost of the divided pressure vessel may be reduced, a pressure vessel may be provided with fewer penetrations through its exterior wall thereby increasing the integrity of the divided pressure vessel, and the divided pressure vessel may have fewer components that are susceptible to failure.

Divided working tanks of the present invention may have various dimensions, as will be understood by those skilled in the art. For a working tank having a cylindrical or cubic interior volume, the working tank has a length, as illustrated by *l* in **Figures 1** and **3**, that is preferably between 24 inches and 120 inches, more preferably between 36 inches and 108 inches, and most preferably between 48 inches and 96 inches. The cylindrical working tank (cubic working tank) has an inside diameter (inside width and/or height), as illustrated by *d* in **Figures 1** and **3**, preferably between 6 inches and 96 inches, more preferably between 12 inches and 84 inches, and most preferably between 18 inches and 48 inches. These preferred ranges may also be used to describe the inside diameter of a divided spherical working tank of the present invention. The ratio of the inside diameter of the cylindrical working tank (width and/or height of the cubic working tank) to the length of the working tank is preferably between 1:1 and 1:5, more preferably between 1:1.25 and 1:4, and most preferably between 1:1.5 and 1:3.

The liquid chambers of divided working tanks of the present invention may have various volumes, as will be understood by those skilled in the art. The volume of a liquid chamber having one or more dividing members but no operating level sensor is measured as the volume of the liquid chamber to the top of the lowest dividing member adjacent that liquid chamber. The volume of a liquid chamber having an operating level sensor positioned therein is measured as the volume maintained using the level sensor. The first liquid chamber has a volume that is preferably between 5 and 250 gallons, more preferably between 10 and 150 gallons, and most preferably between 20 and 75 gallons. The second liquid chamber has a volume that is preferably between 5 and 125 gallons, more preferably between 10 and 75 gallons, and most preferably between 10 and 50 gallons. The third liquid chamber has a volume that is preferably between 5 and 125 gallons, more preferably between 10 and 75 gallons, and most preferably between 10 and 50 gallons. The ratio of the volume of the first liquid chamber to the volume of the second liquid chamber to the volume of the third liquid chamber is preferably between 1:0.1:0.1 and 1:1.5:1.5, more preferably between 1:0.25:0.25 and 1:1:1, and most preferably between



1:0.35:0.35 and 1:0.75:0.75. When the divided working tank is used in a dry cleaning system having a wash tank, the ratio of the volume of the wash tank to the volume of the first liquid chamber to the volume of the second liquid chamber to the volume of the third liquid chamber is preferably between 10:1:0.1:0.1 and 10:20:30:30, more preferably between 10:1.5:0.4:0.4 and 10:10:10:10, and most preferably between 10:2:0.75:0.75 and 10:5:3.5:3.5.

The dividing members of the present invention may have various dimensions, as will be understood by those skilled in the art. While the embodiment of **Figure 1** shows first and second dividing members **120** and **122**, respectively, having the same height, it is to be understood that dividing members of the present invention may have the same or different heights, although dividing members of the same height are preferred. The height of a dividing member is the vertical distance measured from the lowest point of the dividing member to the top of the dividing member, as illustrated by *h* in **Figures 2** and **3**. The height of a dividing member is preferably between 6 and 96 inches, more preferably between 12 and 84 inches, and most preferably between 18 and 48 inches. The ratio of the height of a dividing member to the inside diameter of the cylindrical divided working tank (depth of a cubic divided working tank) is preferably between 0.25:1 and 1:1, more preferably between 0.5:1 and 0.95:1, and most preferably between 0.75:1 and 0.95:1. The longitudinal separation between adjacent dividing members, as illustrated by *x* in **Figures 1** and **3**, is the distance measured from the lowest point of one dividing member to the lowest point of the adjacent dividing member. The longitudinal separation of dividing members of the present invention is preferably between 10 and 100 inches, more preferably between 20 and 80 inches, and most preferably between 30 and 60 inches. The ratio of the longitudinal separation to the inside diameter of the cylindrical working tank (width of the cubic working tank) is preferably between 0.25:1 and 2:1, more preferably between 0.4:1 and 1.5:1, and most preferably between 0.75:1 and 1.25:1.

Referring now to **Figures 3** and **4**, a divided pressure vessel **300** according to the present invention having a cylindrical configuration and a vertical orientation will now be described. The divided pressure vessel **300** has an exterior wall **310** defining an interior volume. While the embodiment illustrated in **Figure 3** shows an exterior wall **310** defining a cylindrical interior volume **318**, it is to be understood that exterior walls of the present invention may define various other shapes of interior volumes including, but not limited to, spherical and cubic.

The components having reference numerals **311-316** and **331-380** may be described and operate in substantially the same manner as the components having reference numerals **111-116** and **131-180** as described above with reference to **Figure 1** and will not be further described.

5 As illustrated in **Figure 3**, a first dividing member **320** extends substantially horizontally from the exterior wall **310**. The first dividing member **320** has a first tubular upright portion **321** extending from a first horizontal portion **322**. The first dividing member **320** defines a first chamber **331**. A second dividing member **325** extends substantially horizontally from the exterior wall **310**. The second dividing member **325** has a second tubular upright portion **326** extending from a second horizontal portion **327**. The second dividing member **325** defines a second chamber **332**. A third chamber **333** is defined by the second end wall member **316** and the side wall member **312**. The first upright portion **321** defines a hole in the first horizontal portion **322** and the second upright portion **326** defines a hole in the second horizontal portion **327** such that the first, the second, and the third chambers **331**, **332**, and **333**, respectively, share a common vapor space **335**. The holes defined by the first and the second upright portions **321** and **326**, respectively, may have various lateral cross-sections. For example, as illustrated in **Figure 4A**, the second tubular upright portion **326** defines a circular hole in the second horizontal portion **327**, and, as illustrated in **Figure 4B**, the first tubular upright portion **321** defines a circular hole in the first horizontal portion **322**. The first and the second dividing members **320** and **325**, respectively, are designed to support the weight of the first and the second treating solutions **341** and **342**, respectively, as will be understood by those skilled in the art. For example, the first and the second dividing members **320** and **325**, respectively, have a thickness that is preferably between about 0.01, 0.1, or 0.125 inch and about 0.25, 0.5, or 1 inch.

While the embodiment illustrated in **Figure 3** shows a second upright portion **326** that is longer than the first upright portion **321**, it is to be understood that first and second upright portions of the present invention may be the same size or may be different sizes, depending, at least in part, on the volume of liquid solution to be contained in the respective chambers. Although the embodiment illustrated in **Figure 3** shows first and second upright portions **321** and **326**, respectively, that are substantially perpendicular to first and second horizontal portions **322** and **327**, respectively, it is to be understood that upright portions of the present invention need

not be perpendicular to horizontal portions. While the embodiment illustrated in **Figure 3** shows a vertically oriented divided pressure vessel **300** having substantially horizontally oriented dividing members **320** and **325**, it is to be understood that vertically oriented divided pressure vessels of the present invention may have dividing members that are oriented other than horizontally. For example, embodiments of vertically oriented dividing members are described above with reference to **Figures 1 and 2**.

Although the embodiment illustrated in **Figure 3** shows first and second dividing members **320** and **325**, respectively, having first and second upright portions **321** and **326**, respectively, that define holes in first and second horizontal portions **322** and **327**, respectively, it is to be understood that dividing members of the present invention may not have upright portions that define holes in horizontal portions, which is to say that horizontal portions of the present invention may be solid. However, if horizontal portions of the present invention are solid, a line or other vapor passage structure should connect the vapor spaces of the adjacent chambers defined by the solid dividing member such that the vapor spaces of the adjacent chambers may not be isolated from one another. Thus, the adjacent chambers will still share a common vapor space.

As will be understood by those skilled in the art, divided pressure vessels of the present invention have exterior walls that are designed to withstand system temperature and pressure. For carbon dioxide based systems that store carbon dioxide solutions at or near saturated conditions, system temperatures may be between about 55 to 62°F (10 to 17°C) at system pressures between about 681 to 756 psig. As divided working tanks of the present invention are capable of storing liquid carbon dioxide, exterior walls of the present invention are capable of withstanding an internal pressure greater than about 500 psig, more preferably greater than about 600 psig, and most preferably greater than about 750 psig. Exterior walls are preferably constructed of metal, more preferably of stainless steel, and most preferably Type 304 stainless steel. However, it is to be understood that the exterior walls according to the present invention may be constructed of various other metals and materials that will withstand system temperature and pressure including, but not limited to, carbon steel, aluminum, ceramics, carbon steel alloys, aluminum alloys, copper alloys, and composite materials.

Dividing members according to the present invention may be constructed of

various materials including, but not limited to, metals, ceramics, plastics, and composite materials. Dividing members are preferably constructed of metal. The metal is preferably selected from the group consisting of stainless steel, aluminum, carbon steel, carbon steel alloys, aluminum alloys, and copper alloys. Dividing members are most preferably constructed of Type 304 stainless steel. Because adjacent chambers share a common vapor space, the liquids in adjacent chambers are maintained at the same pressure. Thus, the dividing members do not form pressure barriers between adjacent chambers. As a result, dividing members of the present invention need not be constructed to withstand the pressure differentials experienced by the exterior walls of the divided pressure vessel. Thus, dividing members may be constructed inexpensively.

Referring now to **Figure 5**, an embodiment of a processing system employing a carbon dioxide solvent and utilizing a divided pressure vessel according to the present invention will now be described. A processing system **500** has a processing vessel **510** in fluid communication with a divided pressure vessel **514**. Vapor fluid communication is provided by vapor transfer system **512** and lines **520** and **522**. Liquid communication is provided by liquid transfer system **516** and lines **524** and **526**. While the embodiment illustrated in **Figure 5** shows a processing system having both a vapor and a liquid transfer system, it is to be understood that processing systems of the present invention may have only a vapor transfer system, or only a liquid transfer system, or may have a fluid transfer system that transfers both vapor and liquid. The vapor transfer system **512** may consist of a line or may comprise various components including, but not limited to, one or more of the following: valves, lines, compressors, condensers, vapor tanks, and moisture separators, among other components. The liquid transfer system **516** may consist of a line or may comprise various components including, but not limited to, one or more of the following: valves, lines, pumps, and filters. As will be understood by those skilled in the art, lines, as used herein, may be selected from the group comprising piping, conduit, and other means of fluid communication that can withstand system temperature and pressure.

As will be understood by one skilled in the art, various processes employing a carbon dioxide solvent may be performed utilizing processing systems according to the present invention including, but not limited to, cleaning, coating, impregnating, extracting, developing, polymer processing, particle processing and purifying and/or

synthesizing chemical compounds. In general, processing systems of the present invention may be particularly suited to performing carbon dioxide based processes that utilize two or more solutions having different compositions. Preferably, the two or more solutions are carbon dioxide based solutions; however, one or more of the

5 solutions may be substantially devoid of liquid carbon dioxide.

Processing systems of the present invention may be used to perform various cleaning processes utilizing a variety of cleaning adjuncts, as will be understood by those skilled in the art. For example, cleaning processes may include the soft and hard cleaning of substrates such as metal, wood, paper, fur, feathers, filtration media,

10 electronics, bio-medical devices/tools/implants, tools, stone and construction materials such as concrete and glass, among others. Cleaning processes may also include the dry cleaning of fabric substrates (*e.g.*, garments, linen, drapery, etc.) and other substrates (*e.g.*, leather) that are typically cleaned in a commercial dry cleaning process (*i.e.*, dry-cleanable articles).

As will be understood by those skilled in the art, processing systems of the present invention may be used to perform various coating processes utilizing a variety of coating adjuncts. For example, coating processes may include coating dry-cleanable articles, and the soft and hard substrates described above, among others. Fabric substrates and leather substrates may be coated with various coating adjuncts

20 such as flame retardants, water repellants, water-resistance agents, water-release agents, sizing agents, sterilizing agents, stain-resistance agents, stain repellants, stain-release agents, anti-bacterial, anti-microbial, anti-viral and other biocide agents, UV resistance agents, and dyes among others. Hard and soft substrates in general may be coated with polymers, as well as many, if not all, of the coatings described for fabric and leather substrates, among other coatings. Electronic substrates may be coated

25 with photoresists, lubricants, insulating layers, conducting layers, polymers, and protecting (*e.g.*, dust resistant) layers, among other coatings.

Processing systems of the present invention may be used to perform various impregnating processes utilizing a variety of impregnating adjuncts, as will be

30 understood by those skilled in the art. For example, materials such as food stuffs and tobacco may be impregnated with flavorings, vitamins, and pharmaceutical compounds, among others; various articles including clothes may be impregnated with perfume, for example; porous materials such as wood, concrete, stone, and brick may be impregnated with insect treatments such as termite repellent,

colorant/pigments such as stains, biocides such as anti-fungal and anti-mildew agents, polymers or other strength enhancers, water repellants, pollution repellants, anti-rot agents, and non-skid agents, just to name a few; bio-medical implants may be impregnated with drugs to provide, for example, controlled release, and anti-bio-  
5 fouling agents, among others; seeds, and agricultural products can be impregnated with insect/fungus protectants, water absorbants, fertilizing agents, and growth hormones, just to name a few; and solid phase chemistry.

As will be understood by those skilled in the art, processing systems of the present invention may be used to perform various extracting processes. For example,  
10 flavors, vitamins, natural product drugs and drug precursors such as taxol and various steroids, oils, cholesterol, toxins and limonene may be extracted from plants, seeds, animal products (e.g., bovine serums and spinal fluids) food products including meat, fish, nuts, eggs, milk and dairy, vegetable juices, fermentation broth, and reaction mixtures, for example.

15 Processing systems of the present invention may be used to perform various developing processes, as will be understood by those skilled in the art. For example, photoresists (microlithography) in semiconductor fabrication, photographic films, and X-ray films may be developed.

As will be understood by those skilled in the art, processing systems of the present invention may be used to perform various polymerizing processes. For  
20 example, polymer synthesis via homogeneous or heterogeneous means may be performed. One or more carbon dioxide based solutions comprising one or more monomers may be combined, in a batch or continuous addition, with one or more carbon dioxide based solutions comprising one or more initiators to form a polymer of  
25 the one or more monomers. The resulting polymer may be soluble or insoluble in liquid carbon dioxide. Preferably, the resulting polymer is insoluble in liquid carbon dioxide. Other polymerizing processes include, but are not limited to, extrusion, fiber spinning, extraction, surface treatments, spraying, and RESS, among others.

Processing systems of the present invention may be used to perform various  
30 purifying processes, as will be understood by those skilled in the art. For example, a compound to be purified may be suspended or dissolved in a first carbon dioxide based treating solution. The compound to be purified may be substantially insoluble in a second treating solution that is substantially devoid of liquid carbon dioxide. The first and the second treating solution may be combined such that the compound to be

purified precipitates out of solution.

As will be understood by those skilled in the art, processing systems of the present invention may be used to perform various synthesizing processes. For example, a first carbon dioxide based reacting solution containing a first reactant may  
5 be combined with a second carbon dioxide based reacting solution containing a second reactant to synthesize a chemical compound. The chemical compound synthesized may be various compounds including, but not limited to, drugs, molecular electronic compounds, fine chemicals, and polymers, among others.

As will be understood by those skilled in the art, processing systems of the  
10 present invention may be used to perform particle processing such as formation and/or coating of drug particles.

Processing systems according to the present invention are preferably carbon dioxide based systems. As used herein, "carbon dioxide based" systems are systems that utilize a solvent comprising greater than 50% carbon dioxide. More particularly,  
15 processing systems according to the present invention are preferably two-phase carbon dioxide based systems. As used herein, "two-phase systems" are systems that have both a liquid and a vapor phase present in the system. The liquid in the two-phase systems may be at saturation conditions or may be sub-cooled. The liquid preferably comprises at least 50% by volume liquid carbon dioxide. The "liquid  
20 phase" may include one or more separate liquid phases in addition to the carbon dioxide liquid phase. For example, the "liquid phase" may include an aqueous phase. The vapor in the two-phase system preferably comprises greater than 75% carbon dioxide vapor, more preferably consists essentially of carbon dioxide vapor, and most preferably consists of carbon dioxide vapor. However, the vapor in the two-phase  
25 system may comprise various gaseous vapors including, but not limited to carbon dioxide, nitrogen, argon, air, helium, ammonia, chlorofluorocarbons, and hydrofluorocarbons. While two-phase systems are preferable, processing systems according to the present invention may employ vapor, liquid, and/or supercritical carbon dioxide based solvents provided that the carbon dioxide based solvent is stored  
30 in the divided pressure vessel as a two-phase system.

Referring now to **Figure 6**, an embodiment of a batch processing system employing a liquid carbon dioxide solution and having a divided working tank will now be described. Valves **601-618** and **660-665** are shut, compressor **652** and pump **655** are secured, and batch tank **654** is pressurized with carbon dioxide vapor. As

illustrated in **Figure 6**, the batch processing system according to an embodiment of the present invention has a working tank **653**. The working tank **653** is a divided pressure vessel, as described above in **Figures 1-4**, having three chambers **A**, **B**, and **C**. Various liquid transfer, re-circulation, and distillation operations will now be described followed by a description of various methods that utilize one or more of these operations. As used herein, the operations of draining, transferring, returning, or distilling a particular solution include draining, transferring, returning, or distilling all or just a portion of the solution, unless otherwise noted.

Liquid may be transferred from chamber **C** of the working tank **653** to the batch tank **654** by opening the valves **615**, **610**, **608**, **601**, and **605**, and starting the pump **655** such that the liquid is transferred through the lines **637**, **636**, **634**, and **632**. Once a desired amount of liquid has been transferred to the batch tank **654**, the pump **655** may be secured and the valves **615**, **610**, **608**, **601**, and **605** may be shut. Liquid may be transferred from the batch tank **654** to chamber **C** of the working tank **653** by opening the valves **611**, **610**, **609**, **616**, **601**, and **605**, and starting the pump **655** such that liquid is transferred through the lines **635**, **634**, **633**, and **641**. Once the desired amount of liquid has been drained from the batch tank **654**, the pump **655** may be secured, and the valves **611**, **610**, **609**, **616**, **601**, and **605** may be shut. Alternatively, liquid may be transferred from the batch tank **654** to chamber **C** of the working tank **653** by opening the valve **665** and gravity draining liquid from the batch tank **654** to chamber **C**. It may be desirable to gravity drain solution from the batch tank **654** to chamber **C** to avoid "contaminating" the pump flow path (lines **633-635**, etc.) with the solution in the batch tank **654**. For example, the solution in the batch tank **654** may be a wash solution that contains one or more aggressive cleaning adjuncts, which work well on cotton fabrics but may harm more delicate fabrics. Gravity draining the wash solution containing aggressive cleaning adjuncts to the working tank may reduce the likelihood that the aggressive cleaning adjuncts "contaminate" the remainder of the system. The aggressive cleaning adjuncts may then be removed from the system by distilling the liquid in chamber **C**.

Liquid in chamber **C** may be distilled by bringing a heating element **658** and a condenser **651** on-line as follows. The valves **618**, **661**, and **662** may be opened. The heating element **658** causes the liquid in chamber **C** to boil or vaporize. Carbon dioxide vapor is transferred through lines **642** and **643** to the condenser **651** where the vapor condenses to form liquid carbon dioxide. The liquid carbon dioxide flows from



the condenser 651 through the line 628 into chamber A of the working tank 653.

When the distillation operation is complete, the valves 662, 661, and 618 may be shut.

The distillate bottoms remaining in chamber C may be purged from the system by opening the valve 614 and draining chamber C to a residue container.

5           Liquid may be circulated through the batch tank 654 and the filter 656 by opening the valves 611, 606, and 608, and starting the pump 655. The filter 656 may include a lint filter and/or a carbon filter. The filter 656 preferably is a combination lint filter and carbon filter configured such that the lint and carbon filters may be operated separately or may be operated together.

10           Liquid may be transferred from chamber B of the working tank 653 to the batch tank 654 by opening the valves 613, 610, 608, 601, and 605, and starting the pump 655 such that liquid is transferred through the lines 639, 636, 634, and 632. Once a desired amount of liquid has been transferred, the pump 655 may be secured and the valves 613, 610, 608, 601, and 605 may be shut. Liquid may be transferred  
15           from the batch tank 654 to chamber B of the working tank 653 by opening the valves 611, 610, 609, 617, 601, and 605, and starting the pump 655. Once the desired amount of liquid is drained from the batch tank 654, the pump 655 may be secured, and the valves 611, 610, 609, 617, 601, and 605 may be shut.

20           Liquid in chamber A of the working tank 653 may be transferred to the batch tank 654 by opening the valves 612, 610, 608, 601, and 605, and starting the pump 655 such that liquid is transferred from chamber A to the batch tank 654 through the lines 640, 636, 634, and 632. Once a desired amount of liquid is transferred to the batch tank 654, the pump 655 may be secured, and the valves 612, 610, 608, 601, and 605 may be shut.

25           Liquid may be transferred from one chamber of the working tank 653 to another chamber of the working tank 653 by opening the respective isolation valves. For example, liquid may be transferred from chamber B to chamber C by opening valves 613 and 615. Liquid levels in two chambers may be equilibrated by opening the respective isolation valves and allowing them to stay open for a sufficient amount  
30           of time, preferably 30 seconds.

          The batch tank 654 may be depressurized by transferring carbon dioxide vapor from the batch tank 654 to the vapor tank 650 and/or venting carbon dioxide vapor to atmosphere. Processed articles or process products may then be removed from the batch tank 654.

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In a first method of operation, the batch process is a cleaning process and the batch tank 654 is a wash tank containing articles to be cleaned. As used herein, the term "cleaning processes" includes various cleaning processes such as commercial dry cleaning processes, among others. Articles to be cleaned are preferably materials such as metal or plastic chip, virgin or recycled paper, glass, microelectronic components, silicon wafers throughout semiconductor (*e.g.*, photolithography) processes, microelectro-mechanical devices (MEMS), fiber-optic devices and components, magnetic storage media, xerography components, metal and/or plastic parts or tools, tubing, pipe, medical devices such as stoppers/scalpels/syringes, medical implants, films such as photography/X-ray/protective films, filter media, slurries, particles, food products, seeds, gels, aerogels, expanded polytetrafluoroethylene (PTFE), open-cell and closed-cell foams, clean-room tools and components, rubber articles and components such as seals (*e.g.*, gaskets and o-rings), packaging for "clean devices" such as microelectronic and medical devices, medical components and foodstuffs, among others. Articles to be dry cleaned (*i.e.*, dry-cleanable articles) are preferably garments, uniforms, protective wear such as fire suits and radioactive protection suits, gloves, blankets and other linen, furs, feathers, structural textiles such as awnings, tents, etc. insulating suits, and sleeping bags, among others. Chamber A contains a solution consisting essentially of liquid carbon dioxide, chamber B contains a wash solution, and chamber C is empty. The wash solution preferably comprises greater than 50% liquid carbon dioxide and a cleaning adjunct. The wash solution preferably comprises between about 0.1, 1, or 5 and about 15, 25, or 49% by volume of the first cleaning adjunct. As will be understood by those skilled in the art, various cleaning adjuncts may be useful in the present invention including, but not limited to, those described in U.S. Patent No. 5,858,022 to Romack et al., U.S. Patent No. 6,001,133 to DeYoung et al., and co-pending and co-assigned U.S. Patent Application Serial No. 09/313,748 to Romack et al. entitled *Combination Surfactant Systems for Use in Carbon Dioxide-Based Cleaning Formulations*, the disclosures of which are hereby incorporated herein in their entireties.

A first volume of the wash solution may be transferred from chamber B to chamber C by opening valves 613 and 615. Preferably, valves 613 and 615 remain open until liquid levels in chambers B and C are equilibrated, and are then shut.

The first volume of wash solution may be used as a pre-wash solution. If used

as a pre-wash solution, the first volume of wash solution is preferably transferred from chamber C to the wash tank 654. If desired, a pre-wash adjunct may be added to the first volume of wash solution before, during, or after transferring the first volume of wash solution from chamber C to the wash tank 654. The pre-wash adjunct is preferably added to the first volume of wash solution while transferring the first volume of wash solution from chamber C to the wash tank 654. The pre-wash solution preferably comprises between about 0.1, 1, or 5 and about 15, 25, or 49% by volume of the pre-wash cleaning adjunct. As will be understood by those skilled in the art, various pre-wash cleaning adjuncts may be useful in the present invention including, but not limited to, the cleaning adjuncts described above. Thus, the pre-wash cleaning adjunct and the cleaning adjunct may be the same or may be different.

After contacting the articles to be cleaned in the wash tank with the pre-wash solution, at least a portion of the pre-wash solution may be returned from the wash tank 654 to the divided working tank 653. Preferably, all of the pre-wash solution is returned to the divided working tank 653. The pre-wash solution may be returned to chamber A, chamber B, or chamber C, or portions of the pre-wash solution may be returned to two or more of these chambers. The pre-wash solution is preferably returned to chamber B or chamber C. More preferably, the pre-wash solution is returned to chamber C, where it is distilled. The distillation operation may be performed during at least one of the operations of transferring wash solution from chamber B to the wash tank 654, washing the articles to be cleaned, returning the wash solution from the wash tank 654 to the divided working tank 653, transferring the rinse solution or the coating solution from chamber C to the wash tank, rinsing or coating the articles, and returning the rinse or coating solution from the wash tank 654 to the divided working tank 653.

A large amount (e.g., greater than 50%) of soils including particulates may be removed from soiled articles within the first few minutes of pre-washing or washing. Pre-washing may remove these soils with a smaller amount of treating solution than washing would use. Additionally, pre-washing may remove the heavy soils before the washing operation and thereby improve cleaning effectiveness. After the pre-wash solution is returned from the wash tank 654 to the divided working tank 653, the wash solution may be transferred from chamber B to the wash tank 654, and the articles to be cleaned may be contacted with the wash solution.

Alternatively, the first volume of wash solution can be held in chamber C and

the wash solution in chamber **B** can be transferred from chamber **C** to the wash tank **654**. A second volume of wash solution can then be transferred from chamber **C** to chamber **B** by opening valves **613** and **615**. Preferably, the second volume of wash solution is transferred from chamber **C** to chamber **B** so that a third volume of wash solution remains in chamber **C**. More preferably, the liquid levels in chamber **B** and chamber **C** are equilibrated. The second volume of wash solution is then transferred from chamber **B** to the wash tank, where the articles to be cleaned are contacted with the wash solution. The third volume of wash solution remaining in chamber **C** is preferably distilled in chamber **C**, and the resulting liquid carbon dioxide is preferably collected in chamber **A**. The distillation operation may be performed during various operations as described above with reference to distillation of the pre-wash solution.

The washing operation preferably includes circulating the wash solution through the wash tank **654** using the pump **655**; however, the wash solution need not be circulated outside of the wash tank **654**. After the article has been contacted with the wash solution for a sufficient amount of time, at least a portion of the wash solution is returned from the wash tank **654** to the divided working tank **653**. Preferably, all of the wash solution is returned from the wash tank **654** to the divided working tank **653**. The wash solution may be returned to chamber **A**, chamber **B**, or chamber **C**, or portions of the wash solution may be transferred to two or more of these chambers. Preferably, the wash solution is returned to chamber **B** or chamber **C**. More preferably, the wash solution is returned to chamber **B**.

The treating solution consisting essentially of liquid carbon dioxide in chamber **A** may be used as a rinse solution. The rinse solution may be transferred from chamber **A** to the wash tank **654** where the articles to be rinsed are contacted with the rinse solution. At least a portion of the rinse solution may be returned from the wash tank **654** to the divided working tank **653**. Preferably, all of the rinse solution is returned from the wash tank **654** to the divided working tank **653**. The rinse solution may be returned to chamber **A**, chamber **B**, or chamber **C**, or portions of the rinse solution may be returned to two or more of these chambers. Preferably, the rinse solution is returned to chamber **B** or chamber **C**. More preferably, the rinse solution is returned to chamber **B**.

The treating solution consisting essentially of liquid carbon dioxide in chamber **A** may also be used as a coating solution. The coating solution is transferred from chamber **A** to the wash tank **654**. A coating adjunct may be added to the coating

solution before, during, or after transferring the coating solution from chamber **A** to the wash tank **654**. Preferably, the coating adjunct is added to the coating solution during or after transferring the coating solution from chamber **A** to the wash tank **654**. More preferably, the coating adjunct is added to the coating solution while the coating solution is being transferred from chamber **A** to the wash tank **654**. The coating solution preferably comprises between about 0.1, 1, or 5 and about 15, 25, or 49% by volume of the coating adjunct. The coating adjunct is preferably suspended in the liquid carbon dioxide by either dissolving or dispersing the coating adjunct into the liquid carbon dioxide. Coating adjuncts that may be used with the present invention include various adjuncts known to those skilled in the art as described above. At least a portion of the coating solution may be returned from the wash tank **654** to the divided working tank **653**. Preferably, all of the coating solution is returned from the wash tank **654** to the divided working tank **653**. The coating solution may be returned to chamber **A**, chamber **B**, or chamber **C**, or portions of the rinse solution may be returned to two or more of these chambers. Preferably, the coating solution is returned to chamber **B** or chamber **C**. More preferably, the rinse solution is returned to chamber **C**.

In another method of operation, the batch process is a purification and isolation process and the batch tank 654 is a purification and isolation tank. Chamber **A** may contain a first solution consisting essentially of liquid carbon dioxide, and preferably contains a solution that consists of liquid carbon dioxide. Chamber **B** may contain a second solution comprising a non-carbon dioxide solvent and a solute to be purified that is substantially insoluble in liquid carbon dioxide. The solute may be suspended (e.g., dissolved or dispersed) in the non-carbon dioxide solvent. The non-carbon dioxide solvent preferably has a higher boiling point than liquid carbon dioxide. Non-carbon dioxide solvents include, but are not limited to water aqueous mixtures (i.e. mixtures preferably comprising greater than 50% water) such as fermentation broth, extraction liquors, homogeneous polymerization mixtures, latexes, emulsions, and biological fluids such as blood, milk, and semen, hydrocarbons and petroleum fluids, halogenated solvents, HFCs, dimethyl sulfoxide (DMSO), terpenes, n-methylpyrrolidone (NMP), ethers, ketones, steam, fuel oils, crude oil, and other densified gases such as helium, nitrogen and air. Solutes to be purified that are substantially insoluble in liquid carbon dioxide include, but are not limited to, plastics, steroids, provitamins, heavy oils and greases, drugs, particulate,

metals and metal complexes, cellulose and cellulose derivatives, proteins, amino acids and natural products.

The second solution comprising the non-carbon dioxide solvent and the solute is transferred from chamber **B** to the purification and isolation tank **654**. The first solution consisting essentially of liquid carbon dioxide is transferred from chamber **A** to the purification and isolation tank **654**. The operation of transferring the first solution from chamber **A** to the purification and isolation tank **654** may be performed before, after, or during the operation of transferring the second solution from chamber **B** to the purification and isolation tank **654**. By combining the first solution with the second solution, at least a portion of the solute precipitates from the second solution. A mixture comprising the first solution and the non-carbon dioxide solvent is drained from the purification and isolation tank **654**. The mixture may further comprise solute, but preferably has a solute concentration of less than 100 ppm. The mixture may be transferred to chamber **C** where it may be distilled, with the liquid carbon dioxide directed to chamber **A**. After the distillation operation is complete, the non-carbon dioxide solvent may be drained from chamber **C** and recycled or discarded.

Referring now to **Figure 7**, a processing system according to the present invention that is useful for purification and isolation will now be described. The purification and isolation system **700** has a pump **710** and a divided pressure vessel **712**. The divided pressure vessel **712** has three chambers, **A**, **B**, and **C**, as described above with reference to **Figures 1-4**. Chamber **C** is used as the batch (purification and isolation) tank and is empty. Chamber **A** contains a first solution that consists essentially of liquid carbon dioxide. Chamber **B** contains a second solution comprising a non carbon-dioxide solvent and a solute that is substantially insoluble in liquid carbon dioxide. Alternatively, chamber **C** may contain the solute and chamber **B** may contain the non-carbon dioxide solvent.

The second solution in chamber **B** may be transferred to chamber **C** by opening the valves **734** and **730** and starting the pump **710** such that solution is transferred through the lines **724**, **728** and **720**. After the desired amount of second solution has been transferred, the pump **710** may be secured and the valves **734** and **730** may be shut. The solute may be suspended in the non-carbon dioxide solvent if it has not already done so. The first solution in chamber **A** may be transferred to chamber **C** by opening the valves **732** and **730** and starting the pump **710** such that solution is transferred through the lines **722**, **728**, and **720**. Once a sufficient amount

of liquid carbon dioxide is transferred to chamber **C**, the pump **710** may be secured and the valves **732** and **730** may be shut. By combining the first liquid and the second liquid, at least a portion of the solute will precipitate from the second solution. A mixture comprising non-carbon dioxide solvent and the first fluid may then be drained  
5 from chamber **C** by opening the valve **736**. The mixture may further comprise solute, and preferably comprises less than 100 ppm solute. The precipitated solute may be removed from chamber **C** and isolated using various processes including, but not limited to, dilution, distillation, filtration, separation, compressed antisolvent, precipitation crystallization, depressurization, centrifugation, electrostatic isolation,  
10 deposition on a substrate, and GAS processes, just to name a few. Optionally, the solute may be rinsed after the draining operation but before the removing operation by opening the valves **732** and **730** and starting the pump **710** to transfer liquid carbon dioxide from chamber **A** into chamber **C**. The rinse solution may be drained from chamber **C** by opening the valve **736**. The purification and isolation system according  
15 to the present invention illustrated in **Figure 7** may be used as part of a larger chemical process, in which case make-up liquid carbon dioxide may be provided into chamber **A** and a feed stream comprising non-carbon dioxide solvent and solute may be provided into chamber **B**.

Referring now to **Figure 8**, a processing system according to embodiments of  
20 the present invention having a divided adjunct addition vessel and a divided waste collection vessel will now be described. The processing system **800** includes a processing vessel **814**. The processing vessel **814** may comprise various processing vessels as will be understood by those skilled in the art including, but not limited to, a cleaning vessel, an etching vessel, a photoresist developing vessel, a photoresist  
25 removing vessel and a chemical mechanical planarization (CMP) vessel. The processing vessel **814** may be configured to perform one or more of the functions of cleaning, etching, developing, photoresist removal and/or chemical mechanical planarization. The processing vessel **814** may be part of a cluster tool apparatus used in the fabrication of microelectronic devices.

30 The processing vessel **814** is in fluid communication with a liquid carbon dioxide storage tank **810** via line **872** and valve **873**. The liquid carbon dioxide storage tank **810** preferably contains or is in communication with heating, cooling and/or pressurization systems capable of maintaining carbon dioxide in the liquid carbon dioxide storage tank **810** in the liquid state. The vapor space of the liquid

carbon dioxide storage tank **810** is in fluid communication with the vapor space of the divided adjunct addition vessel **812** via line **880** and valve **881**. Although not shown in the embodiments illustrated in **Figure 8**, the liquid carbon dioxide storage tank **810** may be in fluid communication with one or more chambers of the divided adjunct  
5 addition vessel **812a -812e** through one or more lines and valves between the liquid space of the liquid carbon dioxide storage tank **810** and the one or more chambers of the divided adjunct addition vessel **812**. Fluid communication between the vapor space of the liquid carbon dioxide storage tank **810** and the divided adjunct addition vessel **812** may be provided to equalize the pressure between the liquid carbon  
10 dioxide storage tank **810** and the divided adjunct addition vessel **812** when an adjunct is introduced into the processing vessel **814** from the divided adjunct addition vessel **812** concurrently with an introduction of liquid carbon dioxide into the processing vessel **814** from the liquid carbon dioxide storage tank **810**. While the embodiments of the processing system **800** illustrated in **Figure 8** show a line **880** and valve **881**  
15 providing fluid communication between the vapor space of the liquid carbon dioxide storage tank **810** and the divided adjunct addition vessel **812**, it is to be understood that processing systems according to the present invention may not have a pressure equalization line. It is also to be understood that processing systems according to the present invention may include a pressurization system in fluid communication with  
20 the divided adjunct addition vessel **812** and capable of pressurizing the divided adjunct addition vessel **812** with, for example, liquid carbon dioxide, carbon dioxide vapor, or a combination of liquid and vapor.

The divided adjunct pressure vessel **812** has a first liquid chamber **812a**, a second liquid chamber **812b**, a third liquid chamber **812c**, a fourth liquid chamber  
25 **812d** and a fifth liquid chamber **812e**. Different adjuncts may be stored in the various chambers of the divided adjunct pressure vessel **812**. For example, when the processing vessel is configured to perform multiple processes in a microelectronic fabrication process, the first liquid chamber **812a** may contain a photoresist developing adjunct, the second liquid chamber **812b** may contain an etching adjunct,  
30 the third liquid chamber **812c** may contain a photoresist removal adjunct, the fourth liquid chamber **812d** may contain a CMP slurry adjunct, and the fifth liquid chamber **812e** may contain a CMP cleaning adjunct.

The first liquid chamber **812a** is in fluid communication with the processing vessel **814** via line **828**, valve **829**, header **819** and line **872**. The second liquid



chamber **812b** is in fluid communication with the processing vessel **814** via line **826**, valve **827**, header **819** and line **872**. The third liquid chamber **812c** is in fluid communication with the processing vessel **814** via line **824**, valve **825**, header **819** and line **872**. The fourth liquid chamber **812d** is in fluid communication with the processing vessel **814** via line **822**, valve **823**, header **819** and line **872**. Finally, the fifth liquid chamber **812e** is in fluid communication with the processing vessel **814** via line **820**, valve **821**, header **819** and line **872**. While the liquid chambers of the divided adjunct addition vessel **812** illustrated in **Figure 8** are in fluid communication with the processing vessel **814** via a common header **819**, it is to be understood that one or more of the liquid chamber of divided adjunct addition vessels of the present invention may be in direct fluid communication (e.g., not via a common header) with the processing vessel. Direct fluid communication may be desirable, for example, when residual adjunct remaining in the header from a previous operation adversely impacts a subsequent operation employing a different adjunct. Although the header **819** as illustrated in **Figure 8** is in fluid communication with the line **872**, it is to be understood that the header (or the lines from one or more of the chambers) may be in direct fluid communication with the processing vessel. Although the processing system **800** shown in **Figure 8** has one divided adjunct addition vessel **812**, it is to be understood that processing systems of the present invention may have more than one divided adjunct addition vessels. While the processing system **800** illustrated in **Figure 8** shows a divided adjunct addition vessel **812** and a liquid carbon dioxide storage vessel **810**, it is to be understood that processing systems according to the present invention may have a divided adjunct addition vessel and no liquid carbon dioxide storage vessel. In these embodiments, the fluids in the one or more chambers of the divided adjunct addition vessel are treating solutions that include liquid carbon dioxide and an adjunct. Although not shown in the embodiments illustrated in **Figure 8**, it is to be understood that one or more pressure-building fluid transfer devices (e.g., pumps) may be present in the lines between divided adjunct addition vessel **812** and processing vessel **814** to overcome a pressure differential in transferring adjuncts to the processing vessel **814**. One skilled in the art will understand how such pressure-building fluid transfer devices may be placed in one or more locations effectively.

The processing vessel **814** is in fluid communication with a divided waste collection vessel **816** via a line **874**. The divided waste collection vessel **816** has a first liquid chamber **816a**, a second liquid chamber **816b**, a third liquid chamber **816c**,

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a fourth liquid chamber **816d**, and a fifth liquid chamber **816e**. The first liquid chamber **816a** is in fluid communication with the line **874** via line **858** and valve **859**. The second liquid chamber **816b** is in fluid communication with the line **874** via line **856** and valve **857**. The third liquid chamber **816c** is in fluid communication with the line **874** via line **854** and valve **855**. The fourth liquid chamber **816d** is in fluid communication with the line **874** via line **852** and valve **853**. The fifth liquid chamber **816e** is in fluid communication with the line **874** via line **850** and valve **851**. While the divided waste collection vessel **816** and the divided adjunct addition vessel **812** as illustrated in **Figure 8** have the same number of liquid chambers, it is to be understood that divided waste collection vessels according to the present invention may have more or less chambers than the adjunct addition vessels. When the divided waste collection vessel **816** has fewer chambers than the divided adjunct addition vessel **812**, it may be desirable to have a discharge line from line **874** to purification system **818** or to a residue receptacle via line **870** and valve **871**. Although the processing system **800** shown in **Figure 8** has one divided waste collection vessel **816**, it is to be understood that processing systems of the present invention may have more than one divided waste collection vessels.

The divided waste collection vessel **816** is in fluid communication with a purification system **818** via line **876**. The purification system **818** may be various purification systems capable of purifying a treating solution in whole or in part as will be understood by those skilled in the art, including, but not limited to, distillation systems, filtration systems, separation systems, absorption systems, depressurization systems, centrifugation systems, or combinations thereof. The first liquid chamber **816a** is in fluid communication with the purification system via line **868**, valve **869**, header **817**, and line **876**. The second liquid chamber **816b** is in fluid communication with the purification system via line **866**, valve **867**, header **817**, and line **876**. The third liquid chamber **816c** is in fluid communication with the purification system via line **864**, valve **865**, header **817**, and line **876**. The fourth liquid chamber **816d** is in fluid communication with the purification system via line **862**, valve **863**, header **817**, and line **876**. The fifth liquid chamber **816e** is in fluid communication with the purification system via line **860**, valve **862**, header **817**, and line **876**. Any of the various waste solutions collected in waste collection vessel **816** may also be discharged to a residue receptacle via line **870** and valve **871** rather than being recycled via the purification system **818**. The purification system **818** is in fluid

communication with the liquid carbon dioxide storage tank **810** via line **878**.

While the processing system **800** as illustrated in **Figure 8** has a divided adjunct addition vessel **812** and a divided waste collection vessel **816**, it is to be understood that processing systems according to the present invention may have a  
5 divided adjunct addition vessel and no divided waste collection vessel, or may have a divided waste collection vessel and no divided adjunct addition vessel. In other embodiments, the processing system may have a divided pressure vessel that serves as a divided adjunct addition vessel and a divided waste collection vessel.

When supercritical processing is desirable in processing vessel **814**, the  
10 processing system **800** may include equipment such as a heat exchanger and/or a pressure-building device for changing the state of liquid carbon dioxide from liquid to supercritical, and may contain equipment such as a throttle valve and/or a heat exchanger for changing the state of the carbon dioxide from supercritical to liquid. Various system configurations may be used as will be understood by those skilled in  
15 the art. For example, a heat exchanger and/or a pressure-building device may be provided in line **872**, and a heat exchanger and/or throttle valve may be provided in line **874**. As another example, the changes of state may be performed in the processing vessel **814**. As yet another example, the changes of state may be performed in the divided adjunct addition vessel **812**. The change of state from a  
20 supercritical fluid-based treating solution to a liquid densified gas-based treating solution may be may result in complete or partial purification of the treating solution such that the change of state operation is also a purification operation.

Various methods according to embodiments of the present invention may be performed utilizing embodiments of the apparatus described with reference to **Figure**  
25 **8**. For example, a method of utilizing a divided storage vessel includes the operations of transferring a first treating adjunct from a first chamber in a divided storage vessel having a plurality of chambers that share a common vapor space to a processing vessel, transferring a densified fluid comprising a liquid densified gas or a supercritical fluid into the processing vessel, removing the first treating adjunct from  
30 the processing vessel, transferring a second treating adjunct having a composition different from the first treating adjunct from a second chamber in the divided storage vessel to the processing vessel, and removing the second treating adjunct from the processing vessel. While listed in a particular order, it is to be understood that these operations may be performed in various orders.

The operations of transferring a first treating adjunct from a first chamber in a divided storage vessel to a processing vessel, and transferring a densified fluid into the processing vessel may occur in various orders. For example, these operations may occur concurrently or one operation may occur before the other operation. The

5 densified fluid may be a liquid densified gas, and the first treating adjunct and the densified fluid may be components of a first treating solution in the first chamber of the divided storage vessel. In this case, the operations of transferring a first treating adjunct from a first chamber in a divided storage vessel to a processing vessel, and transferring a densified fluid into the processing vessel may include the operation of  
10 transferring the first treating solution from the first chamber of the divided storage vessel to the processing vessel.

The operation of transferring a first treating adjunct from a first chamber in the divided storage vessel to a processing vessel may include pressurizing the divided storage vessel to a pressure higher than the pressure of the processing vessel, and  
15 establishing fluid communication between the first chamber in the divided storage vessel and the processing vessel. The operation of pressurizing the divided storage vessel to a pressure higher than the pressure of the processing vessel may include charging carbon dioxide gas and/or liquid or a non-carbon dioxide gas and/or liquid into the divided storage vessel. The operation of removing the first treating adjunct  
20 from the processing vessel may include removing the first treating adjunct and the densified fluid from the processing vessel. The method may further include the operation of transferring a densified fluid into the processing vessel after the operation of transferring a second treating adjunct from the second chamber in the divided storage vessel to the processing vessel.

25 Another method that may be performed according to embodiments of the present invention includes the operations of charging a first densified fluid comprising a liquid densified gas or a supercritical fluid into a processing vessel, removing the first densified fluid from the processing vessel, charging the first densified fluid into a first liquid chamber in a divided storage vessel having a plurality of liquid chambers  
30 that share a common vapor space, charging a second densified fluid comprising a liquid densified gas or a supercritical fluid into the processing vessel, removing the second densified fluid from the processing vessel, and charging the second densified fluid into a second liquid chamber in the divided storage vessel. When the first treating solution is a supercritical fluid based treating solution, the method further

includes changing the state of the first treating solution from supercritical to densified gas prior to charging the first treating solution into the first liquid chamber of the divided storage vessel. When the second treating solution is a supercritical fluid based treating solution, the method further includes changing the state of the second treating solution from supercritical to densified gas prior charging the second treating solution into the second liquid chamber of the divided storage vessel

The method may further include purifying at least one of the first densified fluid and the second densified fluid to provide substantially pure gas or densified fluid after removing the first and/or the second densified fluids to the divided storage vessel. The purifying operation may include transferring at least one of the first densified fluid and the second densified fluid from the divided storage vessel to a purification system, and purifying at least one of the first densified fluid and the second densified fluid to provide gas or densified fluid that is pure or substantially pure.

In the drawings and specification, there have been disclosed typical preferred embodiments of the invention and, although specific terms are employed, they are used in a generic and descriptive sense only and not for purposes of limitation, the scope of the invention being set forth in the following claims.